Effect of the preparation method on low-temperature WGS activity of Cu-Mn spinel oxide catalysts

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Introduction

The Water-Gas Shift Reaction (WGSR) is a well established industrial process for hydrogen generation by conversion of CO in hydrogen-rich gas streams. The need of high-purity hydrogen for fuel cell applications stimulates a great activity in the design of novel, highly active and stable WGS catalysts. Copper is often used as an active component in LT-WGS catalysts. The problem with the tendency of Cu to deactivate could be tackled by applying novel preparation methods. Different synthesis procedures have been employed for preparation of Cu-Mn spinel oxide catalysts [1]. To date, measurements of the WGS activity on combustion-prepared Cu-Mn catalysts in idealized and realistic reformate have not been reported. Recently, some of us have demonstrated that the urea-nitrates combustion method is an attractive technique for preparation of Cu-Mn catalysts with favorable characteristics and catalytic properties for steam reforming of methanol [2]. The aim of this study was to examine the role of the preparation method on the activity of Cu-Mn spinel oxides in the WGSR at low temperature.

Experimental

Two different routes were used for the preparation of $Cu_{0.30}Mn_{0.70}$ catalysts - single-step urea-combustion synthesis (CuMn-CB) and coprecipitation (CuMn-CP). The combustion method involved autoignition of mixed solution of urea with manganese nitrate and copper nitrate (75% excess of urea) in an open muffle furnace (preheated at 400–500 ^{o}C). The coprecipitation took place by mixing aqueous solutions of manganese and copper nitrate with Na_2CO_3, keeping a constant pH value (8.2). After aging, the precipitate was washed, dried and calcined. The catalysts were characterized by N_2 physisorption, XRD, HRTEM, CO-TPR and TPD after CO adsorption and FTIR spectroscopy. The WGS activity was evaluated in a conventional flow reactor at space velocity of 4000 h^{-1} and partial pressure of water vapor equal to 31.1 kPa. The influence of reaction gas mixture, including idealized reformate (4.492 vol.% CO/Ar) and realistic reformate (15 vol.% CO, 10 vol.% CO_2, 63 vol.% H_2, 12 vol. % Ar) were investigated.

Results and discussion

The BET surface area of both Cu-Mn spinel oxide catalysts is quite low (S_{BET} = 5.8 and 5.9 m^2/g for CB- and CP-prepared samples, respectively). XRD patterns of fresh catalysts correspond to the spinel phase $Cu_{1.5}Mn_{1.5}O_4$ and Mn_2O_3. No detectable diffractions of copper

oxide crystallites can be distinguished in both catalysts most probably due to incorporation of the copper ions in the spinel lattice. XRD analysis of used Cu–Mn catalysts showed that the spinel phase has not been completely decomposed after testing under WGSR conditions up to 240 ^{o}C and various $Cu_xMn_yO_z$ spinel phases are still present and co-exist with MnO_x and copper oxide phases. The exact phases are hardly distinguishable due to the presence of many overlapping peaks.

The reduction profiles of Cu–Mn catalysts are very similar and are characterized by a single peak centered at about 450 ^{o}C. The amount of CO consumed during TPR is the same for both samples and corresponds to reduction of both CuO (to Cu^0) and Mn_2O_3 (to MnO). TPD runs after CO adsorption at room temperature showed that: i) no CO adsorbs on pre-oxidized samples; ii) very low amounts of CO are adsorbed on pre-reduced CuMn-CB, while no CO or CO_2 were detected during TPD over CuMn-CP.

The WGS activity of both samples in idealized and realistic reformate (Fig. 1A and B) revealed the superior catalytic performance of combustion-prepared catalyst.

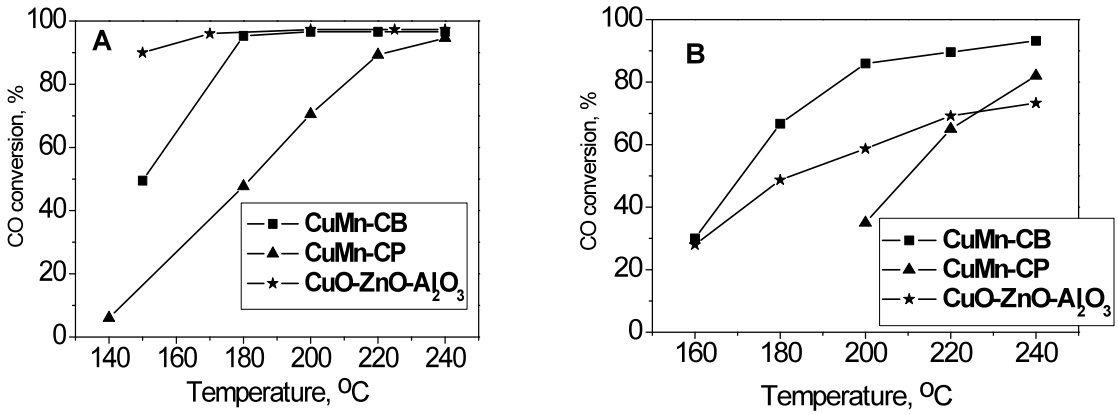

Figure 1. Temperature dependence of CO conversion during WGSR in: A - idealized reformate; B - realistic reformate.

The catalytic performance of Cu-Mn oxide catalysts was compared to commercial low-temperature CuO-ZnO-Al_2O_3. The results indicated that CuMn-CB is more active than commercial sample under realistic conditions.

Catalytic data will be discussed on the basis of HRTEM measurements of the samples before and after catalytic tests and of in situ FTIR spectra in order to explain the strong influence of the preparation method.

Conclusions

The results of a comparative study of two preparation methods demonstrated that combustion synthesis is very suitable method for preparation of active and stable Cu-Mn spinel oxide catalysts for low-temperature WGSR. The comparison with commercial CuO-ZnO-Al_2O_3 revealed the potential applicability of combustion synthesized Cu-Mn spinel oxide catalysts in LT-WGSR.

References

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